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Permeation of Military Fuels Through Nitrile-Coated Fabrics Used for Collapsible Fuel Storage Containers

by James M. Sloan

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14. ABSTRACT

In this report, we compare seven candidate materials for use in collapsible fuel storage tanks. The nitrile composites all consisted of a nylon-woven fabric coated with nitrile rubber on both sides. We evaluated the permeation behavior of these fabrics when challenged with three military different fuels: Jet Propellant 8 (JP-8), diesel fuel, and the American Society for Testing and Materials (ASTM) Reference Fuel B. It was found that the permeation rates for both the JP-8 and diesel fuels were very similar for all nitrile-coated fabrics. When the ASTM Ref Fuel B is used, a significant increase in the permeation rate is observed for five of the candidate fabrics: the Bell Avon, Dunlop, Eng Fabrics, AmFuel, and Reeves fabrics. However, the Zodiac and Pronal nitrile-coated fabrics exhibited only a small increase in permeation rates. This was attributed to a Teflon-like membrane located on the interior side of the coated fabric. When the temperature is raised to 160 $^{\circ}$F, the permeation rates increase by over an order of magnitude for JP-8 and diesel fuels, and by a factor of six for the ASTM Ref Fuel B.

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nitrile rubber, fuel storage, permeation

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1. Introduction

The U.S. Army currently has a large number of fabric reinforced elastomer tanks ranging in size from 100 to 210,000 gallons, used for the storage of fuels and water in the field. Collapsible fuel tanks, fabricated from urethane-coated nylon fabric, were first introduced by the military during the Vietnam conflict. Their performance then, and until recently—particularly in any humid tropic environment—has been less than satisfactory. Unless formulated and produced according to stringent guidelines, urethane-based fabric coatings were extremely susceptible to ultraviolet (UV) radiation and moisture (hydrolytic) degradation (*1*). At that time, these storage tanks were required to contain high-aromatic gasoline as well as diesel and Jet Propellant 8 (JP-8) fuels. The only urethane material that could handle the high-aromatic gasoline fuels was polyester-based urethane, which was prone to hydrolysis. To inhibit hydrolysis, suppliers added chemical stabilizers to the polyester urethanes to prolong the service life. The problem continued resulting in the material degradation and ultimate failure of external tank surfaces and seams, even when protective agents had been incorporated into the tank coatings (*2*). Figure 1 shows a photo of a collapsible fuel storage tank in service. In this photo, wetting of the base textile due to fuel migration between the top and bottom nitrile rubber coating can be seen.

One major change being considered is replacing the elastomeric outer coating of the fabric. The proposed coating is an acrylonitrile polybutadiene (nitrile) rubber-based coating similar to that currently being used in tanks fielded by the United Kingdom (U.K.) forces throughout the world. Nitrile has excellent resistance to oil and gasoline, superior resistance to petroleum-based hydraulic fluids and very good resistance to hydrocarbon solvents (*3–4*). The chemical composition of nitrile allows it to be useful over an extended temperature range (−65−300 °F). The end properties of nitrile rubber can vary according to the amount of acrylonitrile in the polymer backbone (*5*). Increasing acrylonitrile content improves the oil and solvent resistance, while also improving abrasion resistance; while decreasing the amount of acrylonitrile content improves low-temperature flexibility, but increases transport rates of military fuels through the coated fabric (*6*). Often, polyvinyl chloride (PVC) is added to nitrile formulations to improve ozone and weathering properties.

According to the U.K., the nitrile rubber tanks are reported to be providing excellent weathering stability, as well as, increased seam strength. However, these tanks do suffer from an increase in total weight and reduced flexibility, which may influence storage, transportation, and setup of the containers onsite. These storage tanks have demonstrated excellent long-term strength and stability while in service all over the world.

Figure 1. Deployed collapsible fuel storage tank showing fuel infiltration into nylon-woven fabric.

2. Experimental

2.1 Materials

For this study, we obtained currently manufactured nitrile-coated fabrics, as well as several candidate coated fabrics. Samples were obtained from commercial coating sources familiar with fuel storage tank construction and fabrication. Seven nitrile composites were procured and evaluated: Bell Avon (Picayune, MS), Dunlop Textiles (Fife, U.K.), Engineering Fabrics (Rockmart, GA), Zodiac Fabrics Co. (London, Canada), Pronal Elastomer Engineering (Leers, France), Reeves Brothers Inc (Spartanburg, SC) and American Fuel Cells, Bulk Liquid Storage Systems(Mansfield, TX) and Archer Rubber, LLC (Milford, MA) and Coated Fabrics (Magnolia, AR). The nitrile-coated fabric consists of a nylon-woven fabric that is coated on two sides with nitrile rubber to create a rubber composite. Figure 2 shows a micrograph of the side view of this assembly for the Bell Avon nitrile-coated fabric. All manufacturers used nylon as woven fabric. Details as to the coating method were not available. Coatings were all very consistent between manufacturers. Table 1 gives the relevant physical properties of these materials.

2.2 Permeability Measurements

Permeability measurements were determined by monitoring the amount of fuel loss through a flat-planar sheet. This was accomplished by using the American Society for Testing and Materials (ASTM) cup method (*7*). Circular cups were constructed from aluminum and were approximately 4 inches (in) (10.1 cm) wide and 3 in (7.6 cm) deep. The tested specimens measured 5.08 centimeters (2 in) in diameter resulting in an area of 20.25 cm^2. Specimens were clamped to the top of the cell with a retaining ring and sealed with a nylon adhesive. The

reservoir was filled with 1.4 oz of test fuel and the cups inverted so that the liquid fuel directly contacted the specimen. The cells were then allowed to equilibrate for a minimum of 24 hours (h) to attain steady-state permeation. The cells were placed in a high-precision oven and the temperature was kept at either 72 or 160 °F. The precision was +/– 0.5 °F. The cup assemblies were weighted at specific time intervals to determine the weight loss of the permeated fuel. All experiments were run with three specimens from each material. Minor variations, typically +/– 0.005 oz/ft^2/24 h occurred for most of the materials. Figure 3 shows a picture of the cups and a schematic of the fuel cup assembly.
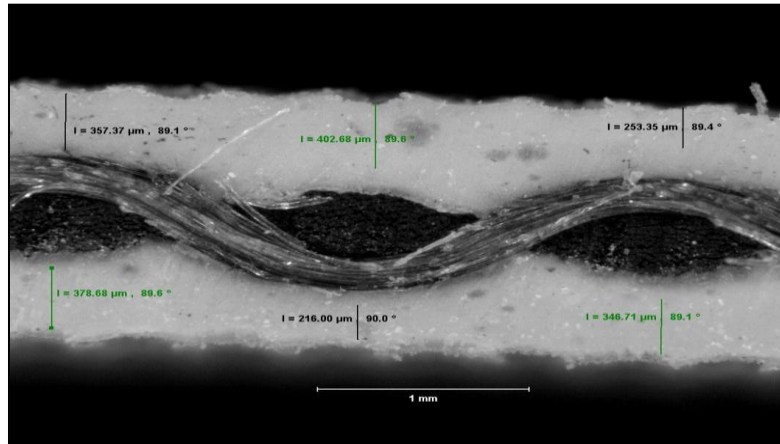
Figure 2. Micrograph of the side view of the nitrile-coated fabric composite.

Table 1. Physical properties for nine nitrile-coated fabrics.

	Fabric Density Oz/yd^2	Coating Thickness (interior) mils	Coating Thickness (exterior) mils
Reeves 18619S	42.1	17.3	16.3
Am Fuel	44.6	18.6	16.1
Archer 4111	46.5	17.9	17.1
Bell Avon	42.4	17.1	16.3
Eng Fabrics	51.9	20.1	20.2
Dunlop	60.5	20.5	20.7
Zodiac	41.3	13.2	13.1
BLSS	43.6	15.4	16.3
Pronal (France)	50.9	17.3	23.2

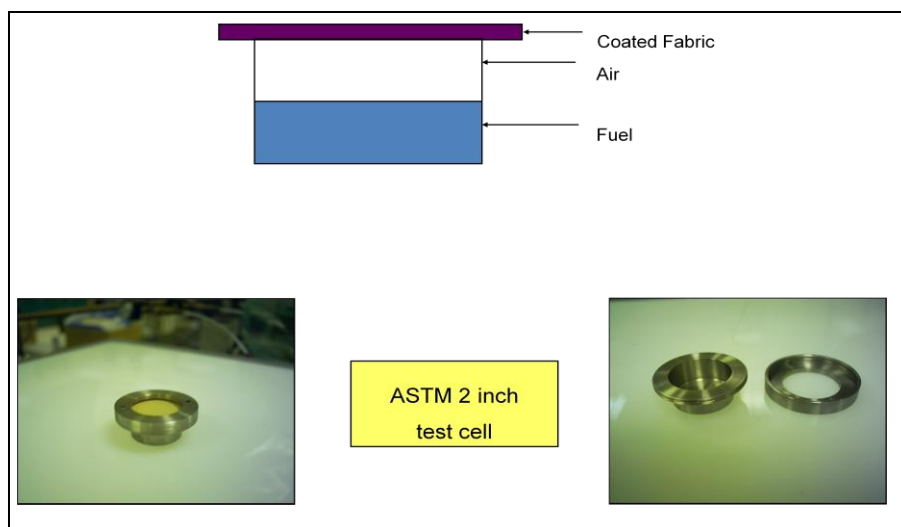Figure 3. ASTM permeation cups.

2.3 Fuels

Three fuels were selected to be used in this study. The first fuel is JP-8, which is an aviation fuel purchased by the military using Purchase Specification MIL-DTL-83133. We obtained JP-8 from the Aberdeen Proving Ground, MD airfield. The second is standard diesel fuel, which is very similar to JP-8—having a similar density but less volatile. From a chemical composition standpoint, JP-8 components consist of C_6–C_{16} hydrocarbons, while diesel fuel consists primarily of slightly heavier C_{10}–C_{21} hydrocarbons. For comparison, we selected ASTM Reference Fuel B, which is a simulant for motor gasoline (MoGas). The U.S. Army is currently considering using collapsible fuel storage containers to store MoGas. ASTM Ref Fuel B is lower in density and is much more volatile than either diesel fuel or JP-8, as it consists of mostly isooctane, a C_8 hydrocarbon. Table 2 shows the densities for these three fuels as well as other common liquids.

Table 2. Vapor pressures of three military fuels and other common liquids.

Chemical	Vapor Pressure (mmHg); 25 $^\circ$C	Vapor Pressure (mmHg); 70 $^\circ$C	Density (g/cm^3)
Diesel Fuel	0.4	5.95	.832
JP-8	0.5	5.75	.82
ASTM Fuel B	41.8	164.50	.748
Water	20.2	79.5	1
Ethanol	43	133.7	.789
Butane	1650	6650	.573
Propane	7600	30600	.20
Gasoline	42	170	.74

2.4 Analysis

Measurement of vapor transmission rate (VTR) is calculated per the testing protocol of ASTM E96 (*7*). ASTM E96 is used to measure the amount of chemical vapor that passes through a polymer membrane in a 24-h period. The permeability of chemical vapor across a polymer membrane can be significantly affected by the chemical vapor pressure (*8–10*).

The fuel diffuses through the film starting at the interior surface and gets desorbed at the exterior surface. The driving force for this permeation is the concentration difference between the interior and the exterior surfaces. The transport of the fuel can be described by Fick's first law (*11*):

$$J = -P \frac{\partial c}{\partial x} \tag{1}$$

Where J is the fuel vapor flux, P is permeability coefficient and $\frac{\partial c}{\partial x}$ is the concentration (c) gradient of the fuel over the film thicknesss (x). One solution to this equation is the use of a psuedosteady-state solution of diffusion in plane-sheet geometry (*12*):

$$\frac{Q_t}{LC_A} = \frac{Pt}{L^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_1^\infty \frac{(-1)^n}{n^2} \exp\left(\frac{Pn^2\pi^2t}{L^2}\right) \tag{2}$$

with the boundary conditions: $C_A \gg C_B$, where C_A and C_B are the concentration of fuel in the donor and receptor compartments, respectively. In equation 2, $Q(t)$ is the total amount of permeating fuel that passes through the membrane in time, t, L is the membrane thickness and D is the fuel-diffusion coefficient. As time approaches infinity, equation 2 simplifies to

$$Q(t) = \frac{PA}{L}\left(t - \frac{L^2}{6D}\right) \tag{3}$$

where A is the cross-sectional area of the membrane (20.26 cm^2). In equation 3, the permeation rate, P, can be determined from the slope of the total amount of fuel permeated versus time.

If you plot the weight loss of the diffusion cups after assembled with coated fabric in place and the reservoir filled with test fuel, you get a curve that is presented in figure 4. The initial portion of this curve, where no weight loss is detectable, is due to the diffusion of the fuel into the coated fabric, where the fuel molecule are entering the coated fabric, but no fuel loss is occurring. When the fabric becomes saturated with fuel and begins to get released at the exterior fabric surface, we see an upturn of the curve, which is a direct measurement of the fuel permeating through the fabric and escaping into the atmosphere. Figure 4 shows graphically how the time lag (time before any mass loss) is measured. At this point, $PA = 0$ and can be related to the diffusion coefficient by the following equation:

$$D = \left(\frac{L^2}{6t}\right) \tag{4}$$

In practice, the total mass loss, Δm, replaces $Q(t)$. The resulting slope of the mass-loss curve will be equal to PA.

The vapor permeation rate (VPR) can be calculated by:

$$VTR = P = \frac{J}{A} = \frac{m}{t \, A} \tag{5}$$

where J has units of $\frac{mass}{time}$.

USED 210K BOTTOM FABRIC BAG A

U 210 B F A - Diffusion/Permeation - Weight Loss from Original Weight: MOGAS - FLUID

$$J = \frac{\partial m}{\partial t}$$

$$D = \frac{l^2}{6 t_{lag}}$$

Weight Loss from Original (gm)

Days at Room Temperature and Humidity

File Name:
USED 210K BOTTOM FABRIC BAG A - MOGAS - Fluid

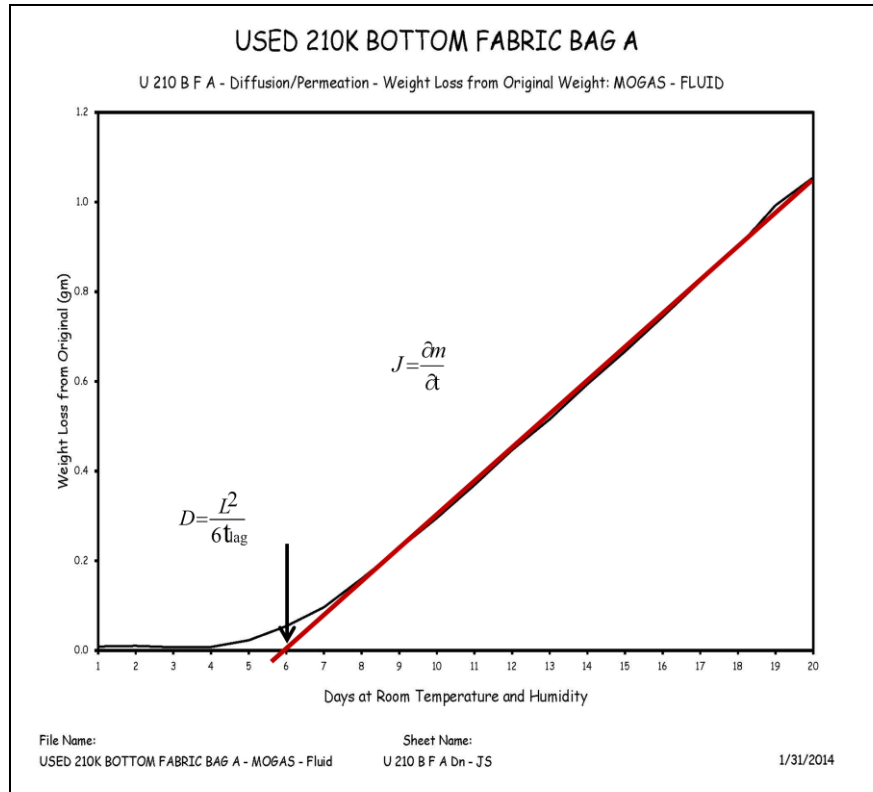Sheet Name:
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Figure 4. Typical plot of cup weight loss over time.

3. Discussion and Results

Figure 5 shows the calculated daily fuel permeation rates for the nine candidate coated fabric materials when challenged with three individual fuels, JP-8, diesel fuel, and ASTM Ref Fuel B. All data were taken at the ambient temperature (72 °F).

For all nine fabrics, the permeation rates for JP-8 and diesel were very similar and very low, measuring below 1 mg/cm^2/24 h. For JP-8 and diesel fuels, six of the fabrics all ranged between 0.17–0.47 mg/cm^2/24 h. For the JP-8 and diesel fuels there were no real differences or trends in the permeation rates measured. The three remaining coated fabric materials—BLSS, Zodiac, and Pronal—exhibited significantly lower permeation rates ranging from 0–0.05 mg/cm^2/24 h. These three materials are constructed with a Teflon[*]-like coating on the interior side of the fuel storage tank. The purchase specification requires 0.035 fl oz/sq ft/24 h, which equals 0.875 mg/cm^2/24 h. In our experiments, all coated fabric composites passed the purchase specification requirement for permeation.

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[*]Teflon is a registered trademark of E. I. du Pont de Nemours and Company.
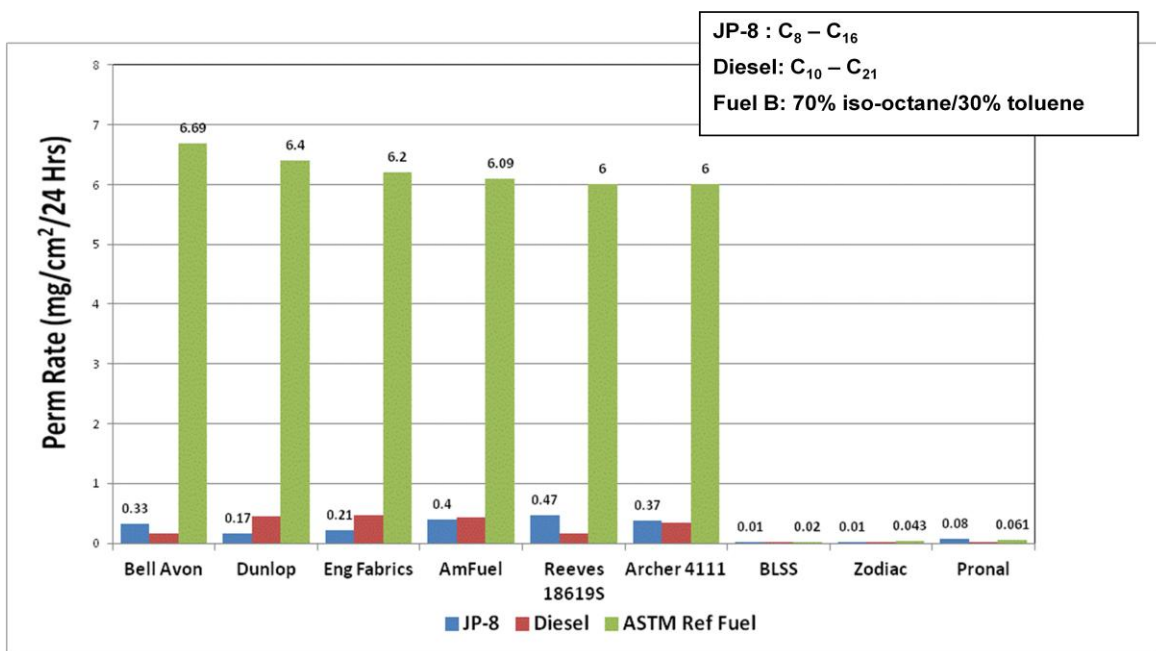
Figure 5. Bar chart comparing the permeation rates of nine nitrile-coated fabric materials when challenged with three separate military fuels.

The permeation rates for the ASTM Ref Fuel B were significantly larger for six of the nine fabrics. The Bell Avon, Dunlop, Eng Fabrics, AmFuel, Archer, and Reeves fabrics produced permeation rates that were 30–50 times larger than diesel fuel when challenged with ASTM Ref Fuel B. The permeation rates for ASTM Ref Fuel B through the Zodiac, BLSS, and Pronal fabrics were surprisingly low, when compared to the JP-8 and diesel results, measuring 2.2 mg/cm^2/24 h and .38 mg/cm^2/24 h, respectively. The interior coating membrane present on theses fabrics is resistant to all military fuels. The net effect is a dramatic decrease in the permeation rate for ASTM Ref Fuel B. The Dunlop fabric used different coatings for their interior and exterior tank system, but no improvement in the permeation rate of any of the fuels was measured.

We summarize the ambient temperature results in table 3. The Zodiac, BLSS, and Pronal JP-8 permeation rates were measured at 0 mg/cm^2/24 h, as no detectable weight loss was measured. With the exception of the three coated fabrics with the interior membrane, the six remaining fabrics would not qualify to contain MoGas in Southwest Asia (SWA).

So the question remains, why does the ASTM Ref Fuel B permeate so much faster than the JP-8 and diesel fuels? One can explain the discrepancy based on the large difference in vapor pressures between the ASTM Ref Fuel B and the JP-8 and diesel fuels. Table 2 presents the vapor pressures for all three fuels, as well as some common commercial liquids used here for comparison. In our experiments, we measure the permeation rate of the vapor that is directly in contact with the nitrile-coated fabric, thus the concentration of fuel vapor on the challenge side of the fabric will significantly affect the overall permeation rate. The vapor pressure is an

indication of a liquid's *evaporation* rate at a given temperature. It relates to the tendency of particles to escape from the liquid. A substance with a high-vapor pressure at normal temperatures is often referred to as *volatile*. The vapor pressure of the ASTM Ref Fuel B is much larger (80 times greater) than the vapor pressure of the JP-8 and diesel fuels. This means that at the same temperature, there is an 80-fold increase in the number of ASTM Ref Fuel B vapor molecules challenging the nitrile-coated fabric surface than the JP-8 and diesel fuels.

Table 3. Effect of military fuel type on the permeation properties of nine nitrile-coated fabrics. Units are mg/cm^2 24 h.

	ASTM Fuel B	JP-8	Diesel
Reeves 18619S	6	0.47	0.16
Am Fuel	6.09	0.4	0.43
Archer 4111	6	0.37	0.35
Bell Avon	6.69	0.33	0.17
Eng Fabrics	6.2	0.21	0.46
Dunlop	6.4	0.17	0.45
Zodiac	.043	001	.02
BLSS	.002	.0002	.0001
Pronal (France)	.061	0.08	.01

Recently, these collapsible fuel storage containers have been deployed in the desert of SWA where surface temperatures can reach up to 180 °F. This makes fabric performance at elevated temperatures a critical physical property in storage tank selection. Figure 6 presents the effect of temperature on the permeation rates of JP-8 through the seven nitrile-coated fabrics. At ambient temperature, small permeation rate differences were observed between all fabrics evaluated in this work. However, when the testing temperature is elevated to 160 °F, as expected, increases in all permeation rates are observed. In the case of the Bell Avon, Dunlop, Eng Fabrics, AmFuel, and Reeves fabrics, an approximate increase of 15 times the ambient temperature permeation is observed. For the Zodiac and Pronal nitrile-coated fabrics, an increase of a factor of two is observed. This is a result of a very effective interior coating located on the interior side of the fabric.

Figure 7 shows very similar behavior for the permeation of diesel fuel though the candidate fabrics. This is not surprising given the similarities in chemical components and vapor pressures between the two fuels.

In figure 8, we present the permeation results for ASTM fuel permeating through seven nitrile-coated fabrics. As previously shown in figures 5 and 6, temperature is an important factor in fuel permeation. At 160 °F, the ASTM fuel permeates at approximately six times the rate measured at ambient temperature. The rate range from 35 mg/cm^2/24 h to 25 mg/cm^2/24 h for the coated fabrics without the interior polymer coating and 6 mg/cm^2/24 h for those coated fabrics that have the coating in place. These are the highest measured values in our study. Even with the materials containing the Teflon coating, these fabrics should not be used for MoGas containment.
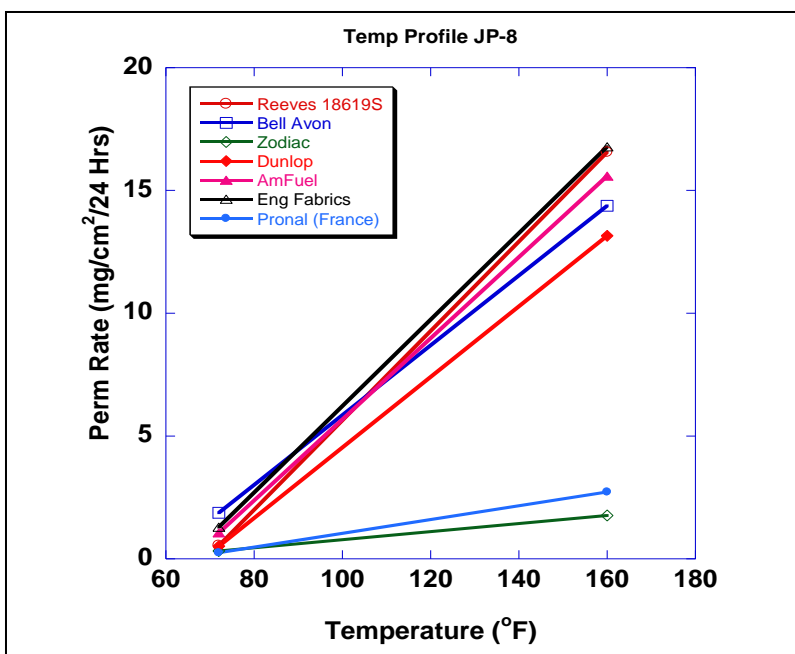

Figure 6. Effect of temperature on the permeation rates of JP-8 through seven nitrile-coated fabrics. Graph only shows the steady-state permeation portion of the curve.
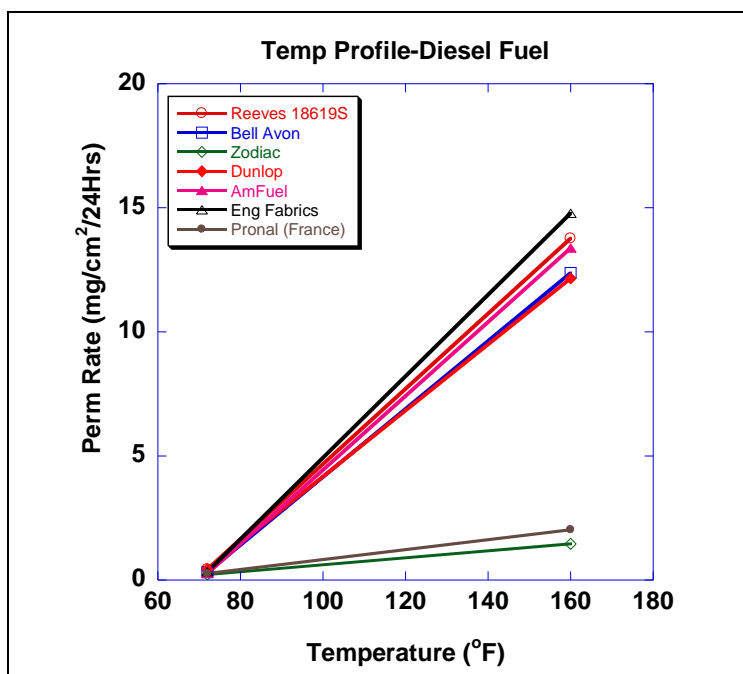
Figure 7. Effect of temperature on the permeation rates of diesel fuel through seven nitrile-coated fabrics. Graph only shows the steady-state permeation portion of the curve.
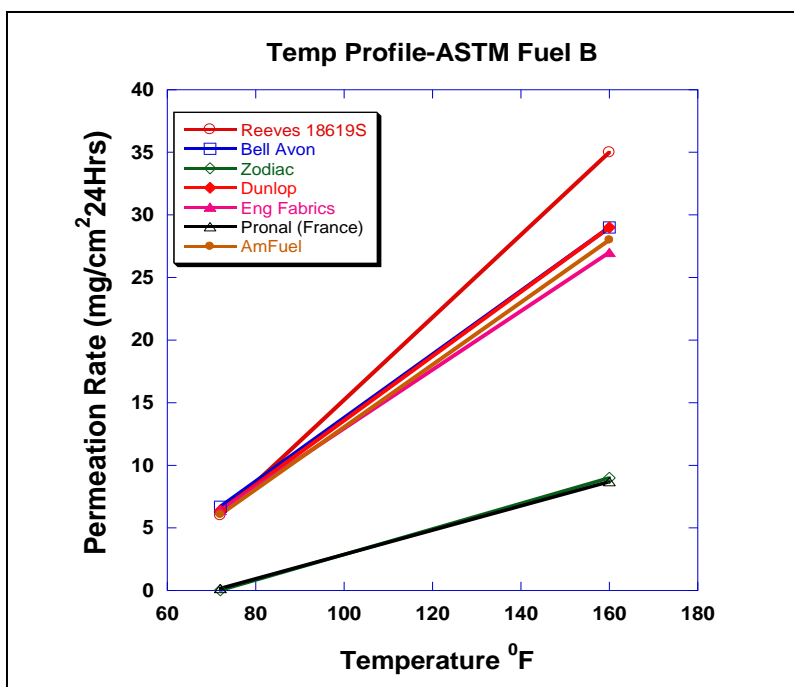

Figure 8. Effect of temperature on the permeation rates of ASTM Ref Fuel B through seven nitrile-coated fabrics. Graph only shows the steady-state permeation portion of the curve.

4. Conclusions

We have evaluated nine currently manufactured nitrile-coated fabrics for use in collapsible fuel storage containers with three different fuels: JP-8, standard diesel, and ASTM Ref Fuel B. Six of the coated-fabric materials—Bell Avon, Dunlop, Engineering Fabrics, Archer, Reeves Bros, and American Fuel—had permeation rates that were nearly identical when challenged with JP-8 and diesel fuels. The Pronal, BLSS, and Zodiac coated fabrics all performed dramatically better due to a Teflon-like interior coating that virtually prevented all fuel permeation.

When ASTM Ref Fuel B was used as the test fuel, a dramatic increase in permeation was measured for six of the coated fabrics. However, similar to the results for the JP-8 and diesel fuels, the Zodiac, Pronal, and BLSS coated fabrics performed very well in our permeation studies.

When the temperature was elevated to 160 °F, significant increases in the permeation rates were measured where the Bell Avon, Dunlop, Engineering Fabrics, Archer, Reeves Bros, and American Fuel increased by a factor 15–20 times above the ambient temperature permeation rates. The Zodiac, Pronal, and BLSS material showed increases of only a factor of six.

5. References

1. Sloan, J.; Flanagan, D.; Deschepper, D.; Pergantis, C.; Touchet, P. Feuer, H. Environmental Aging of Coated Fabric Composites. *Proceedings of the 70th Annual Technical Conference; Society of Plastics Engineers* Vol. 3, pp 789–792, ISBN: 9781622760831, 2012.

2. Sloan, J.; Flanagan, D.; Deschepper, D.; Pergantis, C.; Touchet, P. Feuer, H. Accelerated Environmental Aging of Materials Used for Collapsible Fuel Storage Tanks, ANTEC 2011-*Proceedings of the 69th Annual Technical Conference & Exhibition*, Part 1, p 908, ISBN 9781617829604; 1617829609, 2011.

3. Maria, H.; Lyczko, N.; Nzihou, A.; Mathew, C.; George, S.; Joseph, K. Thomas, S. Transport of Organic Solvents through Natural Rubber/Nitrile Rubber/Organically Modufied Montmorillite Nanocomposites. *J Mater Sci* **2013,** *48*, 5373.

4. Harogoppad, S.; Aminabhavi, T. Diffusion and Sorption of Organic Liquids Through Polymer Membranes. II. Neoprene, SBR, EPDM, NBR and Natural Rubber Versus n-Alkanes. *J Appl Sci* **1991,** *42*, 2329.

5. Linhares, F.; Correa, H. L.; Khalil, C.; Leite, M.; Furtado, C. *Study of the Compatibility of Nitrile Rubber with Brazilian Biodiesel, Energy* **2013,** *49*, 102.

6. Seil, D.; Wolf, F. *Nitrile and Polyacrylic Rubbers, Rubber Technology* **1999,** 322.

7. Spence, K.; Venditti; R.; Rojas, O.et al. *Water Vapor Barrier Properties of Coated and Filled Microfibrillated Cellulose Composite Films, Bioresources* **2011,** *6* (4), 4370.

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List of Symbols, Abbreviations, and Acronyms

ASTM   American Society for Testing and Materials

h   hour(s)

in   inch(es)

JP-8   Jet Propellant 8

MoGas   motor gasoline

PVC   polyvinyl chloride

SWA   Southwest Asia

U.K.   United Kingdom

UV   ultraviolet

VPR   vapor permeation rate

VTR   vapor transmission rate

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